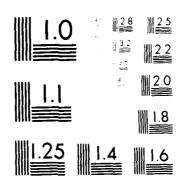
DC CONDUCTIVITY STUDIES OF AN HYDROXIDE ION COMPUTOR AT INTERNEDIATE TEM (U) STANFORD UNIV CA DEPT OF NATERIALS SCIENCE AND ENGINEERING SCROUCH-BAKER ET AL 38 JUL 87 TR-7 F/G 7/4 5-R186 844 1/1 UNCLASSIFIED NL -



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OFFICE OF NAVAL RESEARCH

Contract No. N00014-84-K-0648

Task No. 634-845

Technical Report No. 7

DC Conductivity Studies of an Hydroxide Ion Conductor at Intermediate Temperatures

by

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Submitted to the Journal of the Electrochemical Society

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July 30, 1987

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DC Conductivity Studies of an Hydroxide Ion

Conductor at Intermediate Temperatures

S. Crouch-Baker* and R. A. Huggins*

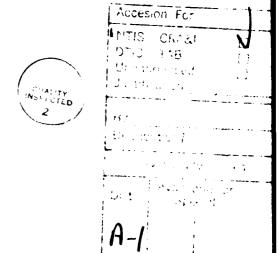
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INTRODUCTION

There is continued interest in the development of an electrochemical process for the production of hydrogen. Much of the current activity in this area involves the development of high temperature steam electrolysis technology operating at about 1000°C, which shows promise for significant reductions in electrical energy requirements compared to traditional water electrolysis at ambient, or near ambient, temperatures. This is due to favorable thermodynamic and kinetic factors at elevated temperatures (1,2). Other commercial approaches have involved the use of systems containing solid ion-exchange polymer electrolytes at 80°C (3). In addition, several proton - conducting solid electrolytes have been investigated that might be useful for this purpose. It has been found, however, that those with the highest conductivity, based upon the transport of protons among donor/acceptor arrays, such as the layered hydrate HUO₂PO₄·4H₂O (HUP) and the beta" aluminas containing H₃O⁺ and/or NH₄+, ions decompose at about 50°C and 200°C, respectively (4,5). There has also been some work on the use of proton conductors based upon doped SrCeO3 in the temperature range 700 - 900°C (6,7). But in this case there is appreciable electronic conductivity at higher temperatures, and the electrolyte resistance is quite high.

On the other hand, it has been pointed out that there would be considerable thermodynamic, as well as practical, advantages if suitable materials could be found that would permit the electrolysis of steam at intermediate temperatures (8). This communication describes the results of some preliminary experiments on an hydroxide ion-conducting electrolyte which may have potential for application in this area.

The ionic conductivity and thermal behaviour of Li₅AlO₄ have previously been studied in both wet and dry environments (9-11). The results of AC conductivity experiments, using silver electrodes, indicated a large increase in the



ionic conductivity of $\text{Li}_5 \text{AlO}_4$ in a wet environment in the temperature range 415 - 450°C. This was not observed in a dry environment. A similar increase was also found with pure LiOH, and it was suggested (10,11) that the large conductivity increase in $\text{Li}_5 \text{AlO}_4$ in a wet environment is due to the formation of LiOH in the grain boundaries, according to the reaction:

 $\text{Li}_5 \text{AlO}_4 + 2 \text{ H}_2 \text{O} = 4 \text{ LiOH} + \text{LiAlO}_2$ In addition, the results of DC polarization experiments were interpreted (9-11) as indicating the presence of appreciable amounts of electronic conduction in some cases.

In this work, the DC conductivity of wet Li₅AlO₄ samples has been measured as a function of temperature and applied voltage. It is proposed that, under the conditions employed in this work, DC charge conduction is due to the transport of hydroxide ions derived from the LiOH contained in the structure, rather than by electronic species.

EXPERIMENTAL METHODS

Li₅AlO₄ was prepared by heating together reagent grade Li₂O and Al₂O₃ in air at 600°C, as described previously (9-11). Disk-shaped samples were prepared by cold-pressing, and they were sintered in air at 600°C prior to use. DC conductivity measurements were made using Pt foil electrodes pressed against the samples, which were held in a glass tube lined with Al foil. At higher voltages, steady values were obtained after only a few minutes. Measurements were carried out in a flowing Ar atmosphere saturated with water.

RESULTS AND DISCUSSION

Fig. 1 shows representative data obtained for the variation of conductivity with reciprocal temperature in the temperature range 390 - 540°C. These data are similar to those obtained previously (9-11), with the conductivity rising sharply in the range 415 - 450°C. It also has been found to rise less steeply above that temperature. However, as shown in that figure, the conductivity depends upon the applied voltage. This relationship is illustrated in Fig. 2 at two different temperatures. It is apparent

^{*}Electrochemical Society Active Member. Key words: conductivity, hydroxide, electrolysis.

that, in this range, the conductivity rises sharply at approximately 1 V and begins to level off at higher voltages. In carrying out these experiments, continuous DC conductance, i.e. without current interruption, was observed for up to ten hours. The results were considerably different when measurements were made in a water-free environment. The initial conductance was lower, and decreased rapidly to negligible values.

The sharp rise in apparent conductivity shown in Fig. 2 is due to a change in the electrode reactions at approximately 1 V. This value corresponds closely to that calculated for the electrolysis of water vapor (1.07 V at 500°C) in the relatively narrow temperature range studied here. Hence, above 1 V the electrode reactions produce and consume OH ions, and are presumed to be:

Negative: $2 H_2O(g) + 2 e^- = 2 OH^- + H_2(g)$

Positive: $2 OH^- = H_2O(g) + 1/2 O_2(g) + 2 e^-$

Thus the overall reaction results in the transport of OH through the electrolyte, presumably with the decomposition of water vapor, leading to the production of hydrogen on the negative electrode side and oxygen on the positive electrode side of the cell.

Hence, such materials show promise as potential electrolytes for the electrolysis of steam at intermediate temperatures. Further studies are underway.

ACKNOWLEDGEMENT

This work was supported, in part, by the Office of Naval Research.

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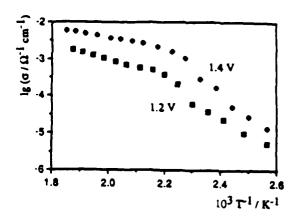


Fig. 1. Variation of DC conductivity with reciprocal temperature for wet Li₅AlO₄. Results are shown for two different applied voltages.

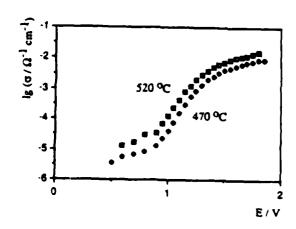


Fig. 2. Variation of DC conductivity with applied voltage, E, for wet Li₅AlO₄. Results are shown for two different temperatures.

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